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MADM—A New Multicomponent Aerosol Dynamics Model

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ABSTRACT. A Multicomponent Aerosol Dynamics Model (MADM) capable of solving the condensation/evaporation equation of atmospheric aerosols is presented. Condensable species may be organic and/or inorganic. For the inorganic constituents the equilibrium model ISORROPIA is used to predict the physical state of the particle, i.e., whether the aerosol is liquid or solid. The mass transfer equations for the fluxes for solid atmospheric particles are developed. MADM is able to simulate aerosol deliquescence, crystallization, solid to solid phase transitions, and acidity transitions. Aerosols of different sizes can be in different physical states (solid, liquid, or partially solid and partially liquid). Novel constraints on the electroneutrality of the species flux between the gas and aerosol phases are presented for both liquid and solid aerosols. These constraints aid in the stability of the algorithm, yet still allow changes in aerosol acidity. As an example, MADM is used to predict the dynamic response of marine aerosol entering an urban area.

INTRODUCTION

Atmospheric aerosols are complex mixtures of inorganic and organic species. The inorganic species include sulfate, nitrate, chloride, ammonium, sodium, and crustal material. At high relative humidity the contribution of inorganic material to the total aerosol mass is enhanced by the existence

of water (Pilinis and Seinfeld 1987, 1988; Kim et al., 1993a, b).

The partitioning of semi-volatile aerosol constituents between the gas and particulate phases is controlled by temperature, gas-phase and aerosol composition. Early aerosol models assumed instantaneous thermodynamic equilibrium for the gas-aerosol partitioning of inorganic species (Pilinis and Seinfeld 1988; Pilinis et al. 1987; Russell et al. 1988). Wexler and Seinfeld

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(1990) evaluated the characteristic time scales for the equilibration of the vapor-phase species with a population of aerosol particles. They found that NH_4NO_3 and NH_4Cl salts might not be at thermodynamic equilibrium with NH_3 , HNO_3 , and HCl vapors, especially under low aerosol loading and low temperatures. In this case both transport and thermodynamics are important for the determination of the concentration of semivolatile ammonium salts. Furthermore, transport time scales are a function of particle diameter. Small particles have greater surface area to mass ratios and thus faster equilibrium time scales than large particles. Wexler and Seinfeld (1990) and Meng and Seinfeld (1996) estimated that micrometer sized particles could require hours or even days to achieve equilibrium with the gas phase. This suggests that large aerosol particles may often exist outside of thermodynamic equilibrium in the atmosphere. This weakness of equilibrium models has been demonstrated during comparisons between the dynamic and equilibrium approaches by Meng et al. (1998) and Capaldo et al. (2000).

Current air quality models that employ equilibrium gas/aerosol mass transfer have difficulties in reproducing observed aerosol distributions of semivolatile constituents. Lurmann et al. (1997) report mean normalized bias in their 24 h average predictions of PM_{10} and $\text{PM}_{2.5}$ for southern California ranging from 6% to 56% for NH_4^+ , NO_3^- , and Cl^- . Lurmann et al. (1997) and Wexler and Seinfeld (1990) suggested that the equilibrium assumption may contribute significantly to these errors. Evaluating this hypothesis requires an aerosol module that treats transport of condensable material accurately. This module should be efficient because the simulation of aerosol dynamics is the slowest part of air quality models (Pilinis and Seinfeld 1988; Jacobson et al. 1996; Nenes et al. 1998).

A number of such aerosol dynamic modules have recently been developed (Meng and Seinfeld 1996; Meng et al. 1998; Jacobson et al. 1996; Jacobson 1997a,b; Sun and Wexler 1998a). Although these each apply fundamental mass transfer equations to liquid aerosol particles, they employ significant simplifications in their representation of solid particles. Meng and Seinfeld (1996) assume that for solids the flux of $\text{HNO}_3(\text{g})$ and $\text{HCl}(\text{g})$ are each coupled to the $\text{NH}_3(\text{g})$ (Wexler and Seinfeld 1990). However, this method does not account for the removal of NO_3^- and Cl^- ions when H_2SO_4 condenses on a solid particle or the interdependence of mass transfer when multiple solid/gas reactions are applied to the same aerosol. Meng et al. (1998) applied this approach in a three-dimensional air-quality model and found parallel processing (5 IBM RS/6000-390 processors) was required to achieve reasonable computation times. Jacobson et al. (1996) and Jacobson (1997a,b) derived analytical approximations for the differential changes in aerosol mass and developed a stable mass transfer algorithm. However, Jacobson et al. (1996) assumed that for solid aerosol the surface vapor pressures can be estimated by assuming that the particles contain a small amount of water. Sun and Wexler (1998a,b) applied a similar approach to solids as Meng and Seinfeld (1996), except that they neglected the interaction of sodium with the fluxes of $\text{HNO}_3(\text{g})$ and $\text{HCl}(\text{g})$. Sun and Wexler (1998a,b) increased the speed of their aerosol module by placing constraints on the fluxes of ionic species when the aerosol phase is near acid neutrality. They neglected, however, the changes in chemistry that occur with small changes in particle acidity.

Even though these previous studies represent significant advances in our ability to model atmospheric aerosol dynamics, they do not present a comprehensive approach

for atmospheric aerosol mass transfer. They may also encounter difficulties with phase transitions between solid and liquid states as well as between neutral and acidic states. In addition, issues of both accuracy and computational efficiency remain to be addressed for the use of such aerosol modules in air quality models. The next step is to develop an aerosol module that can adequately describe the dynamics of both liquid and solid particles. This algorithm should be able to efficiently model phase and acidity transitions as well.

In this paper the Multicomponent Aerosol Dynamics Model (MADM) is presented. This model can be used when the aerosol is an aqueous solution, as well as when the aerosol is a solid particle. For the latter case, new expressions for the fluxes are developed for all possible scenarios of species formation and/or aerosol component substitution.

MODEL DESCRIPTION

Within MADM the population of aerosol particles is represented using the sectional approximation (Gelbard and Seinfeld 1980; Warren and Seinfeld 1990) common in aerosol air quality models (Pilinis and Seinfeld 1988; Meng et al. 1998). This involves using discrete aerosol size sections and considering the particles in a size section to be internally mixed (all homogeneous in composition). A moving sectional approach is then used allowing the diameter of the aerosol section to change as evaporation and condensation affect the size of the aerosol particles. The modified aerosol size sections can then be mapped to the original aerosol sections using spline techniques if necessary (Gelbard et al. 1980).

Gas-Aerosol Transport Processes

The flux, J_{ik} , of a species i from the gas phase to an aerosol size section k has the

following general form:

$$J_{ik} = 2\pi D_i D_{pk} N_k f(Kn_{ik}, a_{ik}) [c_i - c_{ik}^{eq} \eta_k], \quad (1)$$

where D_i is the diffusivity of i in air, D_{pk} is the characteristic diameter of the particles in section k , N_k is the number density of particles in section k , and $f(Kn_{ik}, a_{ik})$ is the correction for noncontinuum effects and imperfect accommodation (Dahneke 1983). Kn_{ik} is the Knudsen number and a_{ik} is the accommodation coefficient for species i and section k . The bulk gas-phase concentration is c_i , and c_{ik}^{eq} is the gas-phase concentration of i that would be at equilibrium with the aerosol composition of section k . The Kelvin effect correction for section k is η_k . In this work an accommodation coefficient of 0.1 is used for all condensable species and the Kelvin effect is neglected since only particles > 0.05 microns are considered. A positive flux J_{ik} describes condensation of i from the gas phase to the aerosol section k , and a negative J_{ik} describes evaporation.

At any given time, aerosol particles may contain water or they may be completely dry. The existence of water in the particulate phase depends on the ambient temperature and relative humidity, as well as the composition of the particle. In MADM, the amount of water and the aerosol physical state are determined by the thermodynamic equilibrium model ISORROPIA (Nenes et al. 1998). If the aerosol particles are liquid, the equilibrium concentration c_{ik}^{eq} in the above equation can be evaluated based on the aqueous phase composition and thermodynamics (Nenes et al. 1998). If the aerosol particles are solid, c_{ik}^{eq} is calculated using the algorithm described below. The sulfuric acid equilibrium concentration at the surface of an aerosol is very low and is considered zero in MADM.

A system of ordinary differential equations (ODEs) is generated if Equation (1) is applied to each aerosol size section and each aerosol species. MADM numerically solves this system in order to predict the dynamic behavior of the gas and aerosol phases. The system of ODEs is integrated using the double precision version of LSODE, the Livermore solver for stiff ODEs (Hindmarsh 1983). A relative tolerance of 10^{-4} and an absolute tolerance of $10^{-8} \mu\text{g m}^{-3}$ are used for all species.

Dynamics of a Liquid Particle

The simplicity of Equation (1) is confounded by the stiffness (and resulting computational expense) that occurs because the fluxes of dissociating species (HNO_3 , NH_3 , H_2SO_4 , and HCl) have a strong impact on aerosol acidity and thus equilibrium thermodynamics. For instance, if the aerosol and gas phases are at equilibrium and the air parcel $\text{H}_2\text{SO}_4(\text{g})$ concentration increases, then some of the added $\text{H}_2\text{SO}_4(\text{g})$ will enter the aerosol phase. This small addition of sulfate will cause a significant increase in the aerosol acidity (Sun and Wexler 1998a). As a result, volatile acidic aerosol species (NO_3^- and Cl^-) will evaporate and the basic gas NH_3 will condense. Because numerical solutions to systems of differential equations use discrete time steps, oscillations will occur between states that are slightly more alkaline and slightly more acidic than equilibrium requires. These oscillations can become unstable because of asymmetry regarding limiting assumptions for condensation versus evaporation. For a severe condensation driving force the flux is limited by the species diffusion rate through the gas phase (i.e., c_{ik}^{eq} has a lower bound of 0). On the other hand, the equivalent physical constraints for species evaporative flux are ne-

glected (i.e., interparticle diffusion and establishment of near-particle steady-state gas-phase concentration profiles) since these processes have characteristic time scales several orders of magnitude faster than gas phase diffusion (Wexler and Seinfeld 1990). The result is that c_{ik}^{eq} has an infinite upper bound. Under these conditions, ensuring stable numerical behavior for realistic atmospheric perturbations requires very tight numerical integration tolerances for dissociating species and is thus computationally expensive.

To avoid this problem Sun and Wexler (1998a,b) coupled the acid ($\text{HNO}_3(\text{g})$, $\text{H}_2\text{SO}_4(\text{g})$, and $\text{HCl}(\text{g})$) and base ($\text{NH}_3(\text{g})$) fluxes to ensure that equal quantities of acid and base are transferred between the aerosol and gas phases. Their constraint, however, neglects the interdependence of the acid fluxes and it does not allow the $p\text{H}$ of the particle to change as the influencing gas-phase concentrations change. This constraint on the aerosol $p\text{H}$ may lead to inaccuracies if applied to environments that are ammonia poor because $p\text{H}$ has a significant effect on the equilibrium concentrations.

MADM improves upon this approach by considering the thermodynamic relationships between acid fluxes and allowing small changes in the acidity of the particle up to a critical acidity flux of α_k (in $\mu\text{moles m}^{-3} \text{ s}^{-1}$ for aerosol size section k). First, for a given section, k , the net H^+ flux, $J_{\text{H}^+,k}$, is evaluated by assuming full dissociation of transferred $\text{HNO}_3(\text{g})$, $\text{H}_2\text{SO}_4(\text{g})$, $\text{HCl}(\text{g})$, and $\text{NH}_3(\text{g})$ to form NO_3^- , SO_4^{2-} , Cl^- , and NH_4^+ , respectively.

$$J_{\text{H}^+,k} = J_{\text{HNO}_3,k} + J_{\text{HCl},k} + 2J_{\text{H}_2\text{SO}_4,k} - J_{\text{NH}_3,k} \quad (2)$$

If $J_{\text{H}^+,k}$ is $> \alpha_k$ or $< -\alpha_k$, then $J_{\text{H}^+,k}$ is restricted to one of these limits by modification of c_{ik}^{eq} for HNO_3 , HCl , and NH_3 by

a correction factor Q_k such that $c_{\text{HNO}_3k}^{eq*} = Q_k c_{\text{HNO}_3k}^{eq}$, $c_{\text{HCl}k}^{eq*} = Q_k c_{\text{HCl}k}^{eq}$, and $c_{\text{NH}_3k}^{eq*} = c_{\text{NH}_3k}^{eq}/Q_k$. This scheme maintains the gas-phase products $c_{\text{HNO}_3}^{eq}$, $c_{\text{NH}_3}^{eq}$, c_{HCl}^{eq} , $c_{\text{NH}_3}^{eq}$, and $c_{\text{HCl}}^{eq}/c_{\text{HNO}_3}^{eq}$ that are predicted by the thermodynamics of the system.

To calculate Q_k , Equations (1) and (2) are combined replacing c_{ik}^{eq} with c_{ik}^{eq*} for HNO_3 , HCl , and NH_3 and $J_{\text{H}+,k}$ with $\pm \alpha_k$ ($+\alpha_k$ if $J_{\text{H}+,k}$ is positive in Equation (2) and $-\alpha_k$ if $J_{\text{H}+,k}$ is negative) to give

$$Q_k = \frac{-\beta + \sqrt{\beta^2 + 4\eta_k^2 D'_{\text{NH}_3k} c_{\text{NH}_3k}^{eq} (D'_{\text{HNO}_3k} c_{\text{HNO}_3k}^{eq} + D'_{\text{HCl}k} c_{\text{HCl}k}^{eq})}}{2\eta_k (D'_{\text{HNO}_3k} c_{\text{HNO}_3k}^{eq} + D'_{\text{HCl}k} c_{\text{HCl}k}^{eq})}, \quad (4)$$

where

$$\begin{aligned} \beta = & D'_{\text{NH}_3k} c_{\text{NH}_3} - D'_{\text{HNO}_3k} c_{\text{HNO}_3} \\ & - 2D'_{\text{H}_2\text{SO}_4k} c_{\text{H}_2\text{SO}_4} - D'_{\text{HCl}k} c_{\text{HCl}} \\ & + \alpha_k \frac{(-1)^x}{2\pi D_{pk} N_k}. \end{aligned} \quad (5)$$

In Equations (4) and (5) the concentrations c_i and c_{ik}^{eq} are in $\mu\text{moles m}^{-3}$, $D'_{ik} = D_i f(Kn_{ik}, a_{ik})$ with D_i in $\text{m}^2 \text{s}^{-1}$ and f defined as in Equation (1), α_k is in $\mu\text{moles m}^{-3} \text{s}^{-1}$, D_{pk} is the diameter in meters, N_k is the number density of particles per m^3 , and η_k is the Kelvin effect for section k . In Equation (5), x is 1 if $J_{\text{H}+,k}$ is negative (Equation (2)) and x is 2 if $J_{\text{H}+}$ is positive.

Several special conditions exist where Equation (3) is not applicable. If $c_{\text{NH}_3}^{eq}$ is 0 and β is negative, then the correction factor, Q_k , can be calculated by

$$Q_k = \frac{-\beta}{(D'_{\text{HNO}_3k} c_{\text{HNO}_3k}^{eq} + D'_{\text{HCl}k} c_{\text{HCl}k}^{eq}) \eta_k}. \quad (6)$$

$$\begin{aligned} & \alpha_k (-1)^x \\ & = 2\pi D'_{\text{HNO}_3} D_{pk} N_k [c_{\text{HNO}_3} - Q_k c_{\text{HNO}_3}^{eq} \eta_k] \\ & \quad + 2\pi D'_{\text{HCl}} D_{pk} N_k [c_{\text{HCl}} - Q_k c_{\text{HCl}}^{eq} \eta_k] \\ & \quad + 4\pi D'_{\text{H}_2\text{SO}_4} D_{pk} N_k c_{\text{H}_2\text{SO}_4} \\ & \quad - 2\pi D'_{\text{NH}_3} D_{pk} N_k \left[c_{\text{NH}_3} - \frac{c_{\text{NH}_3}^{eq}}{Q_k} \eta_k \right]. \end{aligned} \quad (3)$$

Solving for Q_k

If $c_{\text{HNO}_3}^{eq}$ and c_{HCl}^{eq} are 0 and β is positive, Q_k can be determined by

$$Q_k = \frac{D'_{\text{NH}_3k} c_{\text{NH}_3k}^{eq} \eta_k}{\beta}. \quad (7)$$

If $c_{\text{NH}_3}^{eq}$ is 0 and β is positive or if $c_{\text{HNO}_3}^{eq}$ and c_{HCl}^{eq} are 0 and β is negative, then no correction is made ($Q_k = 1$). These last two cases are not likely to lead to severe oscillations because they represent conditions where condensation, which is limited by the gas-phase diffusion rate, is dominant in the system.

By allowing α_k to vary proportionally (by the constant A) with the aerosol hydrogen ion concentration, $c_{\text{H}+,k}$,

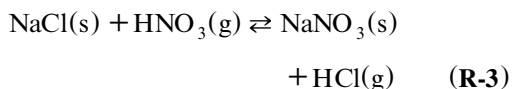
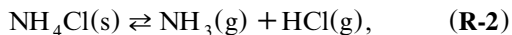
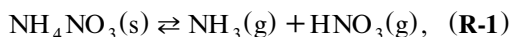
$$\alpha_k = A c_{\text{H}+,k}, \quad (8)$$

the acid flux constraint can be applied to acidic, neutral, and alkaline particles without imposing disproportionate flux restrictions in any of these cases. The advantage of this scheme over that of Sun and Wexler (1998a) is that particle acidity is allowed to vary as required by thermodynamics; yet at

the same time, numerical instability is avoided. For this work a proportionality constant of $A = 0.1 \text{ s}^{-1}$ is used. This value of A is low enough to restrict numerical oscillations, but high enough to allow acidification (or neutralization) of a particle in a few seconds. This time scale for acidification is likely to be adequate given atmospheric time scales for emissions and gas-phase reactions involving $\text{H}_2\text{SO}_4(\text{g})$, $\text{HNO}_3(\text{g})$, $\text{HCl}(\text{g})$, and $\text{NH}_3(\text{g})$. Sensitivity model runs for the scenario presented below indicate that values of A between 0.01 and 1.0 yield similar results.

Solid Aerosol Dynamics

As in the liquid case, if the aerosol particles are solid, all terms in Equation (1) can be easily estimated with the exception of c_{ik}^{eq} . In contrast to the liquid calculation, however, the equilibrium gas-phase concentrations over the solid particle surface cannot be determined based on the aerosol-phase information only. This is because equilibrium concentrations are independent of the amounts of existing solids. To resolve this issue Wexler and Seinfeld (1990) and Meng and Seinfeld (1996) assumed that the dominant solid aerosol-phase/gas-phase reactions



can be applied independently. They calculated electroneutral mass transfer (if $\text{NH}_3(\text{g})$ was present) to a pure solid particle and then added the fluxes for the three equations. This decoupling of the driving forces for mass transfer may introduce errors when multiple reactions are important.

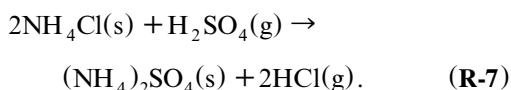
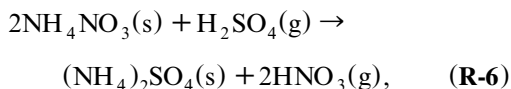
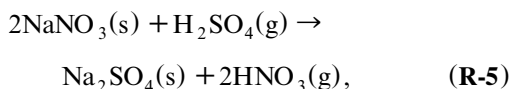
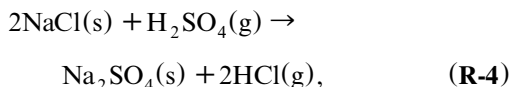
In contrast, MADM solves for the fluxes of HNO_3 , HCl , and NH_3 by considering reactions (R-1)–(R-3) simultaneously with the addition of an electroneutrality (Equation (9)) constraint (if $\text{NH}_3(\text{g})$ is present) on the molar fluxes, J_i , of HNO_3 , H_2SO_4 , HCl , and NH_3

$$J_{\text{NH}_3} = J_{\text{HNO}_3} + J_{\text{HCl}} + 2J_{\text{H}_2\text{SO}_4}. \quad (9)$$

Changes in particle acidity do not have to be considered in the solid aerosol, as was the case in the liquid aerosol, because the aerosol species can be assumed to exist as neutral salts (e.g., $\text{NH}_4\text{NO}_3(\text{s})$). However, difficulty arises from the fact that during the lifetime of an atmospheric particle, phase transitions may occur, e.g., $\text{NH}_4\text{NO}_3(\text{s})$ may evaporate completely or $\text{NaNO}_3(\text{s})$ may form. These solid-phase transitions lead to a new chemical composition, and therefore it is necessary to solve a new system of equations. To account for these transitions, MADM tests for phase changes during integration by calculating the internal aerosol composition (via ISORROPIA, Nenes et al. 1998) every time the integration routine requires J . The appropriate reactions (and system of equations) for the given aerosol state are thus chosen “continuously.” Since the existence of a specific inorganic solid in the particulate phase depends on the relative amounts of ammonium, sulfate, and sodium (Pilinis and Seinfeld 1987; Nenes et al. 1998), differential equations are derived for all the subcases listed in Nenes et al. (1998). These subcases are defined by the relevant chemical reactions that apply to the system.

If there is sufficient ammonia to maintain a neutral aerosol phase, MADM considers the three reversible reactions shown above (R-1)–(R-3). These reactions determine the equilibrium concentrations of ammonia, nitric acid, and hydrochloric acid over the particle surface. The first reaction

(R-1) is considered "active" if either $\text{NH}_4\text{NO}_3(\text{s})$ exists in the aerosol phase or sufficient $\text{NH}_3(\text{g})$ and $\text{HNO}_3(\text{g})$ are present that $\text{NH}_4\text{NO}_3(\text{s})$ will be formed (i.e., the product of $c_{\text{HNO}_3} c_{\text{NH}_3}$ exceeds the equilibrium constant for reaction (R-1), K_1). Application of the second reaction requires either the presence of aerosol NH_4Cl or sufficient $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$ that $\text{NH}_4\text{Cl}(\text{s})$ will be formed ($c_{\text{HNO}_3} c_{\text{NH}_3} > K_2$). The third reaction is "active" if $\text{NaCl}(\text{s})$ exists and $c_{\text{HCl}}/c_{\text{HNO}_3} < K_3$ or $\text{NaNO}_3(\text{s})$ exists and $c_{\text{HCl}}/c_{\text{HNO}_3} > K_3$. In addition to these reactions there are four practically irreversible reactions. These occur during $\text{H}_2\text{SO}_4(\text{g})$ condensation and convert nitrate and chloride salts to sulfate ones.



In addition, if $\text{H}_2\text{SO}_4(\text{g})$ and $\text{NH}_3(\text{g})$ condense on a particle that contains both $\text{NaCl}(\text{s})$ and $\text{NaNO}_3(\text{s})$, thermodynamics favors the formation of $\text{Na}_2\text{SO}_4(\text{s})$ and $\text{NH}_4\text{Cl}(\text{s})$. Thermodynamics also prevents the occurrence of all four nitrate and chloride salts ($\text{NaNO}_3(\text{s})$, $\text{NaCl}(\text{s})$, $\text{NH}_4\text{NO}_3(\text{s})$, and $\text{NH}_4\text{Cl}(\text{s})$). MADM assumes that sodium will preferentially associate with the nitrate (i.e., either $\text{NaNO}_3(\text{s})$, $\text{NaCl}(\text{s})$, and $\text{NH}_4\text{Cl}(\text{s})$ will exist or $\text{NaNO}_3(\text{s})$, $\text{NH}_4\text{NO}_3(\text{s})$, and $\text{NH}_4\text{Cl}(\text{s})$ will exist). These solid-phase assumptions and reactions (R-4)–(R-7) affect the aerosol composition and therefore the equilibrium concentra-

tions of the system. For this reason they need to be considered when deciding which of equilibrium reactions (R-1), (R-2), and (R-3) are "active" in controlling the c_{ik}^{eq} values. For example, if $\text{NaCl}(\text{s})$ is present and $\text{H}_2\text{SO}_4(\text{g})$ and $\text{NH}_3(\text{g})$ condense, then $\text{NH}_4\text{Cl}(\text{s})$ is assumed to form and (R-2) is considered "active."

When there is not enough ammonia to neutralize the aerosol sulfate, the salts of nitrate and chloride will not be present in the aerosol. Therefore, none of the above reactions are "active." The cases where the available sulfate is fully neutralized are presented first, followed by the solid acidic state.

Neutral solid aerosol. In these cases the atmospheric system contains enough ammonia and sodium to neutralize the available sulfate. The possible solids (neglecting the formation of double salts) in the aerosol phase are $(\text{NH}_4)_2\text{SO}_4(\text{s})$, $\text{NH}_4\text{NO}_3(\text{s})$, $\text{NH}_4\text{Cl}(\text{s})$, $\text{NaCl}(\text{s})$, $\text{NaNO}_3(\text{s})$, and $\text{Na}_2\text{SO}_4(\text{s})$. However, the four chloride and nitrate salts cannot coexist. This leads to separate treatment of systems involving some fraction of these salts (subcases (a)-(i)). The sulfate solids, $(\text{NH}_4)_2\text{SO}_4(\text{s})$ and $\text{Na}_2\text{SO}_4(\text{s})$, are assumed to have negligible vapor pressures and therefore their concentrations can be determined by stoichiometry. A summary of the solid neutral aerosol subcases is presented in Table 1. The aerosol and gas-phase compositions for each subcase are presented in Table 2.

(a) *Sodium and NH_4Cl equilibrium reactions, (R-2) and (R-3), are active.* This subcase applies to the aerosol and gas-phase compositions shown in Table 2. In general these conditions involve $\text{NH}_4\text{Cl}(\text{s})$, $\text{NaCl}(\text{s})$, and $\text{NaNO}_3(\text{s})$ with the absence of $\text{NH}_4\text{NO}_3(\text{s})$. $\text{NH}_4\text{Cl}(\text{s})$, $\text{NaCl}(\text{s})$, and $\text{NaNO}_3(\text{s})$ can be absent if gas-phase concentrations of HNO_3 , NH_3 , HCl , or H_2SO_4 favor their

TABLE 1. Solid aerosol neutral subcases of MADM.

Subcase	Active* Equilibrium Reactions and Flux Constraints [†]	Equations
For all cases, $J_i = 2\pi D_i D_p N f(K n_i, a_i) [c_i - c_i^{eq} \eta]$ for $i = \text{HNO}_3$, NH_3 , and HCl unless otherwise stated below with c_i^{eq} given below and $J_{\text{H}_2\text{SO}_4} = 2\pi D_{\text{H}_2\text{SO}_4} D_p N f(K n_{\text{H}_2\text{SO}_4}, a_{\text{H}_2\text{SO}_4}) [c_{\text{H}_2\text{SO}_4}]$		
(a)	$\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HCl(g)}$ $\text{NaCl(s)} + \text{HNO}_3\text{(g)} \rightleftharpoons \text{NaNO}_3\text{(s)} + \text{HCl(g)}$	$c_{\text{HNO}_3}^{eq} = \frac{-V + [V^2 + 4D'_{\text{NH}_3} K_2 (D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}}) / K_3]^{1/2}}{2(D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}})}$ $c_{\text{NH}_3}^{eq} = \frac{K_2}{K_3 c_{\text{HNO}_3}^{eq}}$ $c_{\text{HCl}}^{eq} = K_3 c_{\text{HNO}_3}^{eq}$ $V = D'_{\text{NH}_3} c_{\text{NH}_3} - D'_{\text{HNO}_3} c_{\text{HNO}_3} - D'_{\text{HCl}} c_{\text{HCl}} - 2D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4}$
(b)	$\text{NH}_4\text{NO}_3\text{(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HNO}_3\text{(g)}$ $\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HCl(g)}$	$c_{\text{HNO}_3}^{eq} = \frac{-V + [V^2 + 4D'_{\text{NH}_3} K_1 (D'_{\text{HNO}_3} + K_2 D'_{\text{HCl}} / K_1)]^{1/2}}{2(D'_{\text{HNO}_3} + K_2 D'_{\text{HCl}} / K_1)}$ $c_{\text{NH}_3}^{eq} = \frac{K_1}{c_{\text{HNO}_3}^{eq}}$ $c_{\text{HCl}}^{eq} = \frac{K_2}{K_1} c_{\text{HNO}_3}^{eq}$ $V = D'_{\text{NH}_3} c_{\text{NH}_3} - D'_{\text{HNO}_3} c_{\text{HNO}_3} - D'_{\text{HCl}} c_{\text{HCl}} - 2D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4}$
(c)	$\text{NH}_4\text{NO}_3\text{(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HNO}_3\text{(g)}$ $\text{NaCl(s)} + \text{HNO}_3\text{(g)} \rightleftharpoons \text{NaNO}_3\text{(s)} + \text{HCl(g)}$	$c_{\text{HNO}_3}^{eq} = \frac{-V + [V^2 + 4D'_{\text{NH}_3} K_1 (D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}})]^{1/2}}{2(D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}})}$ $c_{\text{NH}_3}^{eq} = \frac{K_1}{c_{\text{HNO}_3}^{eq}}$ $c_{\text{HCl}}^{eq} = K_3 c_{\text{HNO}_3}^{eq}$ $V = D'_{\text{NH}_3} c_{\text{NH}_3} - D'_{\text{HNO}_3} c_{\text{HNO}_3} - D'_{\text{HCl}} c_{\text{HCl}} - 2D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4}$
(d)	None	$J_{\text{NH}_3} = 2J_{\text{H}_2\text{SO}_4}, J_{\text{HCl}} = J_{\text{HNO}_3} = 0$
(e)	$\text{NH}_4\text{NO}_3\text{(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HNO}_3\text{(g)}$	$c_{\text{HNO}_3}^{eq} = \frac{-P + [P^2 + 4D'_{\text{NH}_3} D'_{\text{HNO}_3} K_1]^{1/2}}{2D'_{\text{HNO}_3}}$ $c_{\text{NH}_3}^{eq} = \frac{K_1}{c_{\text{HNO}_3}^{eq}}$ $J_{\text{HCl}} = 0$ $P = D'_{\text{NH}_3} c_{\text{NH}_3} - D'_{\text{HNO}_3} c_{\text{HNO}_3} - 2D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4}$
(f)	$\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HCl(g)}$	$J_{\text{HNO}_3} = 0$ $c_{\text{NH}_3}^{eq} = \frac{-R + [R^2 + 4D'_{\text{NH}_3} D'_{\text{HCl}} K_2]^{1/2}}{2D'_{\text{NH}_3}}$ $c_{\text{HCl}}^{eq} = \frac{K_2}{c_{\text{NH}_3}^{eq}}$ $R = D'_{\text{HCl}} c_{\text{HCl}} + 2D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4} - D'_{\text{NH}_3} c_{\text{NH}_3}$

TABLE 1. (Continued)

Subcase	Active* Equilibrium Reactions and Flux Constraints†	Equations
(g)	$\text{NaCl(s)} + \text{HNO}_3\text{(g)} \rightleftharpoons \text{NaNO}_3\text{(s)} + \text{HCl(g)}$ $J_{\text{NH}_3} = 0$	$c_{\text{HNO}_3}^{eq} = \frac{S}{D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}}}$ $J_{\text{NH}_3} = 0$ $c_{\text{HCl}}^{eq} = K_3 c_{\text{HNO}_3}^{eq}$ $S = D'_{\text{HCl}} c_{\text{HCl}} + 2 D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4} + D'_{\text{HNO}_3} c_{\text{HNO}_3}$
(h)	$J_{\text{NH}_3} = 0$	$J_{\text{HNO}_3} = J_{\text{NH}_3} = 0$ $J_{\text{HCl}} = -2 J_{\text{H}_2\text{SO}_4}$
(i)	$J_{\text{NH}_3} = 0$	$J_{\text{HNO}_3} = -2 J_{\text{H}_2\text{SO}_4}$ $J_{\text{NH}_3} = J_{\text{HCl}} = 0$

* An active reaction is one in which reactants exist for the thermodynamically favored reaction direction (forward or reverse) as determined by the gas phase concentrations.

† Flux constraints are applied only if an equilibrium reaction is restricted because a nonexistent species is being required to evaporate. See text and Table 2 for the cases that require flux constraints.

formation. For example, if only NaCl(s) and NH₄Cl(s) exist in the aerosol phase and $c_{\text{HCl}}/c_{\text{HNO}_3} < K_3$, then (R-3) is active and will form NaNO₃(s).

Additional aerosol and gas-phase compositions are included in this subcase to improve the computational efficiency of the algorithm. For example, consider the case where only NaCl(s) and NaNO₃(s) exist in the aerosol phase. If H₂SO₄(g) condenses it will displace some of the available chloride. This chloride has the potential to react with gas-phase ammonia to form NH₄Cl(s). Anticipating this potential NH₄Cl(s) formation, the NaCl(s) and NaNO₃(s) case is grouped in subcase (a). If NH₄Cl(s) is not formed, then the predicted flux of ammonia, J_{NH_3} , will be negative (NH₃(g) evaporates) and subcase (g) is applied where only reaction (R-3) is active and the ammonia flux is set to 0. If this is not done, and the NaCl(s) and NaNO₃(s) case is treated from the beginning with only the application of reaction (R-3), then oscillations may develop between NH₄Cl(s) being formed from

H₂SO₄(g) condensation and evaporation of NH₄Cl(s) that may occur when the newly formed NH₄Cl(s) is subjected to the application of reaction (R-2) in subcase (a). To avoid these oscillations, the more comprehensive set of reactions (subcase (a)) is first applied. Then if one of the assumed active reactions cannot achieve its equilibrium value (for instance a nonexistent species is predicted to evaporate), that reaction is “deactivated” and the appropriate subset of the former reactions is applied. Similar cases of “special applications” of a subcase are discussed in the footnotes of Table 2.

In this case the following equilibrium relations hold:

$$K_2 = c_{\text{NH}_3}^{eq} c_{\text{HCl}}^{eq}, \quad (10)$$

$$K_3 = \frac{c_{\text{HCl}}^{eq}}{c_{\text{HNO}_3}^{eq}}, \quad (11)$$

where K_i is the thermodynamic rate constant for the i th chemical reaction. Com-

binning Equations (10) and (11),

$$c_{\text{NH}_3}^{eq} = \frac{K_2}{K_3 c_{\text{HNO}_3}^{eq}}. \tag{12}$$

In addition to the above equations, the fluxes of ammonia, nitric acid, hydrochloric acid, and sulfuric acid must satisfy electroneutrality (Equation (9)). Equations (1), (9), (11), and (12) can be solved to give the equilibrium concentration for $\text{HNO}_3(\text{g})$:

$$c_{\text{HNO}_3}^{eq} = \frac{-V + \left[V^2 + 4D'_{\text{NH}_3} \times K_2 (D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}}) / K_3 \right]^{1/2}}{2(D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}})}, \tag{13}$$

where

$$V = D'_{\text{NH}_3} c_{\text{NH}_3} - D'_{\text{HNO}_3} c_{\text{HNO}_3} - D'_{\text{HCl}} c_{\text{HCl}} - 2D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4} \tag{14}$$

with $D'_i = D_i f(Kn, a_i)$ the effective diffusivity for all condensable gases i . Equations (1) and (11)–(14) provide a self-consistent method for the calculation of the mass transfer of the inorganic species between the gas and the aerosol phases for this subcase.

(b) NH_4NO_3 and NH_4Cl equilibrium reactions, (R-1) and (R-2), are active. In

TABLE 2. Inorganic aerosol species and gas-phase concentration products that apply to each solid neutral subcase.

Aerosol species	$c_{\text{NH}_3} c_{\text{HNO}_3} > K_1?$	$c_{\text{NH}_3} c_{\text{HCl}} > K_2?$	$c_{\text{HCl}} / c_{\text{HNO}_3} > K_3?$	Note
Subcase (a)				
NaCl, NaNO ₃ , NH ₄ Cl	—	—	—	
NaCl, NaNO ₃ , NH ₄ Cl, Na ₂ SO ₄	—	—	—	
NaCl, NH ₄ Cl	—	—	No	
NaCl, NH ₄ Cl, Na ₂ SO ₄	—	—	No	
Special applications of subcase (a)				
NaCl	—	—	No	1,2
NaCl, Na ₂ SO ₄	—	—	No	1,2
NaCl, NaNO ₃	—	—	—	1,2
NaCl, NaNO ₃ , Na ₂ SO ₄	—	—	—	1,2
NaNO ₃	No	—	Yes	1,3
NaNO ₃ , Na ₂ SO ₄	No	—	Yes	1,3
Subcase (b)				
NH ₄ NO ₃ , NH ₄ Cl	—	—	—	
NH ₄ NO ₃ , NH ₄ Cl, (NH ₄) ₂ SO ₄	—	—	—	
NH ₄ NO ₃ , NH ₄ Cl, Na ₂ SO ₄	—	—	—	
NH ₄ NO ₃ , NH ₄ Cl, Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	—	—	—	
NH ₄ Cl	Yes	—	—	
NH ₄ Cl, (NH ₄) ₂ SO ₄	Yes	—	—	
NH ₄ Cl, Na ₂ SO ₄	Yes	—	—	
NH ₄ Cl, Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	Yes	—	—	
NH ₄ NO ₃	—	Yes	—	
NH ₄ NO ₃ , (NH ₄) ₂ SO ₄	—	Yes	—	
NH ₄ NO ₃ , Na ₂ SO ₄	—	Yes	—	
NH ₄ NO ₃ , Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	—	Yes	—	
None	Yes	Yes	—	
(NH ₄) ₂ SO ₄	Yes	Yes	—	
Na ₂ SO ₄	Yes	Yes	—	
Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	Yes	Yes	—	

TABLE 2. (Continued)

Aerosol species	$c_{\text{NH}_3}c_{\text{HNO}_3} > K_1?$	$c_{\text{NH}_3}c_{\text{HCl}} > K_2?$	$c_{\text{HCl}}/c_{\text{HNO}_3} > K_3?$	Note
<i>Special applications of subcase (b)</i>				
NaNO ₃	—	Yes	No	1
NaNO ₃ , Na ₂ SO ₄	—	Yes	No	1
NaNO ₃ , NH ₄ Cl	—	—	No	1
NaNO ₃ , NH ₄ NO ₃ , Na ₂ SO ₄	—	—	No	1
NaNO ₃ , NH ₄ NO ₃	—	No	Yes	1, 4
NaNO ₃ , NH ₄ NO ₃ , Na ₂ SO ₄	—	No	Yes	1, 4
NaNO ₃ , NH ₄ NO ₃	—	Yes	—	4
NaNO ₃ , NH ₄ NO ₃ , Na ₂ SO ₄	—	Yes	—	4
NaNO ₃ , NH ₄ NO ₃ , NH ₄ Cl	—	—	—	4
NaNO ₃ , NH ₄ NO ₃ , NH ₄ Cl, Na ₂ SO ₄	—	—	—	4
<i>Special applications of subcase (c)</i>				
NaNO ₃	Yes	—	Yes	1, 5
NaNO ₃ , Na ₂ SO ₄	Yes	—	Yes	1, 5
Subcase (d)				
None	No	No	—	
(NH ₄) ₂ SO ₄	No	No	—	
Na ₂ SO ₄	No	No	—	
Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	No	No	—	
Subcase (e)				
NH ₄ NO ₃	—	No	—	
NH ₄ NO ₃ , (NH ₄) ₂ SO ₄	—	No	—	
NH ₄ NO ₃ , Na ₂ SO ₄	—	No	—	
NH ₄ NO ₃ , Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	—	No	—	
NaNO ₃ , NH ₄ NO ₃	—	No	No	
NaNO ₃ , NH ₄ NO ₃ , NaSO ₄	—	No	No	
None	Yes	No	—	
(NH ₄) ₂ SO ₄	Yes	No	—	
Na ₂ SO ₄	Yes	No	—	
Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	Yes	No	—	
<i>Special applications of subcase (e)</i>				
NaNO ₃	—	No	No	1, 6
NaNO ₃ , Na ₂ SO ₄	—	No	No	1, 6
Subcase (f)				
None	No	Yes	—	
(NH ₄) ₂ SO ₄	No	Yes	—	
Na ₂ SO ₄	No	Yes	—	
Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	No	Yes	—	
NH ₄ Cl	No	—	—	
NH ₄ Cl, (NH ₄) ₂ SO ₄	No	—	—	
NH ₄ Cl, Na ₂ SO ₄	No	—	—	
NH ₄ Cl, Na ₂ SO ₄ , (NH ₄) ₂ SO ₄	No	—	—	
<i>Special applications of subcase (f)</i>				
NaCl	—	—	Yes	1, 7, 8
NaCl, Na ₂ SO ₄	—	—	Yes	1, 7, 8
NaCl, NH ₄ Cl	—	—	Yes	7
NaCl, NH ₄ Cl, Na ₂ SO ₄	—	—	Yes	7

TABLE 2. (Continued)

Aerosol species	$c_{\text{NH}_3} c_{\text{HNO}_3} > K_1?$	$c_{\text{NH}_3} c_{\text{HCl}} > K_2?$	$c_{\text{HCl}} / c_{\text{HNO}_3} > K_3?$	Note
<i>Special applications of subcase (g)</i>				
NaCl	No	No	No	9
NaCl, Na ₂ SO ₄	No	No	No	9
NaCl, NaNO ₃	No	No	—	9
NaCl, NaNO ₃ , Na ₂ SO ₄	No	No	—	9
<i>Special applications of subcase (h)</i>				
NaCl	—	No	Yes	10
NaCl, Na ₂ SO ₄	—	No	Yes	10
<i>Special applications of subcase (i)</i>				
NaNO ₃	No	No	No	11
NaNO ₃ , Na ₂ SO ₄	No	No	No	11

—Indicates that the truth of the statement is not relevant.

1 H₂SO₄(g) and NH₃(g) condensation may cause the formation of NH₄Cl(s) if NaCl(s) exists or is expected to form by reaction (R-3) or may cause the formation of NH₄NO₃(s) if NaNO₃(s) is present and NaCl(s) is absent.

2 If upon solving this case NH₃(g) is determined to evaporate from the aerosol phase ($J_{\text{NH}_3} < 0$), then NH₄Cl(s) will not form (reaction (R-2) should not be active) and subcase (g) applies.

3 If upon solving this case $J_{\text{NH}_3} > J_{\text{HCl}}$, then NH₄NO₃(s) forms and NaCl(s) does not. Therefore, reaction (R-2) is active and (R-3) is not and so subcase (b) is applied.

4 Assumes that any NaCl(s) that forms will react with NH₄NO₃(s) to form NH₄Cl(s).

5 If upon solving this case NH₃(g) is determined to condense ($J_{\text{NH}_3} > 0$), then NH₄NO₃(s) forms and subcase (b) is applied. If NH₃(g) is determined to evaporate from the aerosol phase ($J_{\text{NH}_3} < 0$), then NaCl(s) forms and subcase (a) is applied.

6 If upon solving this case NH₃(g) is determined to evaporate from the aerosol phase ($J_{\text{NH}_3} < 0$), then NH₄NO₃(s) will not form (reaction (R-1) should not be active) and subcase (i) applies.

7 Assumes that any NH₄NO₃(s) that forms will react with NaCl(s) to form NH₄Cl(s) and NaNO₃(s) and that the NaNO₃(s) that forms will be consumed by the sodium reaction (R-3).

8 If upon solving this case NH₃(g) is determined to evaporate from the aerosol phase ($J_{\text{NH}_3} < 0$), then NH₄Cl(s) will not form (reaction (R-2) should not be active) and subcase (h) applies.

9 Only applies if subcase (a) indicates that no ammonia will condense.

10 Only applies if subcase (f) indicates that no ammonia will condense. Also, assumes that any NH₄NO₃(s) that forms will react with NaCl(s) to form NH₄Cl(s) and NaNO₃(s) and that both the NH₄Cl(s) and NaNO₃(s) that form will be consumed by the reactions (R-2) and (R-3), respectively.

11 Only applies if subcase (e) indicates that no ammonia will condense.

general this subcase involves particles of NH₄NO₃(s) and NH₄Cl(s) (Table 2). Either or both of NH₄NO₃(s) and NH₄Cl(s) may be absent if gas-phase concentrations of HNO₃, NH₃, and/or HCl promote their formation. A number of special cases are also treated with this subcase to improve computational efficiency. Following the same procedure as in the previous case, we can solve for the equilibrium concentrations of the volatile inorganic species.

Specifically,

$$c_{\text{HCl}}^{eq} = \frac{K_2}{K_1} c_{\text{HNO}_3}^{eq}, \quad (15)$$

$$c_{\text{NH}_3}^{eq} = \frac{K_1}{c_{\text{HNO}_3}^{eq}}, \quad (16)$$

$$c_{\text{HNO}_3}^{eq} = \frac{-V + [V^2 + 4D'_{\text{NH}_3} \times K_1(D'_{\text{HNO}_3} + K_2 D'_{\text{HCl}})/K_1]^{1/2}}{2(D'_{\text{HNO}_3} + K_2 D'_{\text{HCl}}/K_1)}. \quad (17)$$

Equations (1) and (14)–(17) are used to calculate the mass transfer of the inorganic species between the gas and the aerosol phases for this subcase.

(c) *Sodium and NH_4NO_3 equilibrium reactions, (R-1) and (R-3), are active.* Because an aerosol composition of sodium nitrate and ammonium chloride is thermodynamically favored over a composition of sodium chloride and ammonium nitrate, MADM assumes that NaCl(s) and $\text{NH}_4\text{NO}_3\text{(s)}$ will not exist in a particle at the same time. This limits the application of subcase (c) to the following scenario. Only $\text{NaNO}_3\text{(s)}$ or $\text{NaNO}_3\text{(s)}$ and $\text{Na}_2\text{SO}_4\text{(s)}$ exists in the aerosol phase; $c_{\text{HNO}_3} c_{\text{NH}_3} > K_1$, which implies that $\text{NH}_4\text{NO}_3\text{(s)}$ will form and (R-1) is active; and $c_{\text{HCl}}/c_{\text{HNO}_3} > K_3$, which implies that NaCl(s) will form and (R-3) is active. Since NaCl(s) and $\text{NH}_4\text{NO}_3\text{(s)}$ cannot coexist, subcase (c) is only used to determine which species (NaCl(s) or $\text{NH}_4\text{NO}_3\text{(s)}$) is likely to form.

Following the same procedure as in the previous case, one can solve for the equilibrium concentrations of the volatile inorganic species. Specifically,

$$c_{\text{HCl}}^{eq} = K_3 c_{\text{HNO}_3}^{eq}, \quad (18)$$

$$c_{\text{NH}_3}^{eq} = \frac{K_1}{c_{\text{HNO}_3}^{eq}}, \quad (19)$$

$$c_{\text{HNO}_3}^{eq} = \frac{-V + \left[V^2 + 4D'_{\text{NH}_3} \times K_1 (D'_{\text{HNO}_3} + K_2 D'_{\text{HCl}}) \right]^{1/2}}{2(D'_{\text{HNO}_3} + K_2 D'_{\text{HCl}})}. \quad (20)$$

Equations (1), (14), and (18)–(20) are used to calculate the mass transfer of the inorganic species between the gas and the aerosol phases for this subcase. If this system predicts the condensation of $\text{HNO}_3\text{(g)}$, then $\text{NH}_4\text{NO}_3\text{(s)}$ will be present and subcase (b) should be used, otherwise NaCl(s)

will form and subcase (a) is appropriate. In no situation is subcase (c) used to determine final c_{ik}^{eq} values since MADM assumes that $\text{NH}_4\text{NO}_3\text{(s)}$ and NaCl(s) cannot coexist.

(d) *$\text{NH}_4\text{NO}_3\text{(s)}$, $\text{NH}_4\text{Cl(s)}$, NaCl(s) , and $\text{NaNO}_3\text{(s)}$ do not exist in the aerosol phase.* In this subcase the aerosol consists only of $\text{Na}_2\text{SO}_4\text{(s)}$ and/or $(\text{NH}_4)_2\text{SO}_4\text{(s)}$ as inorganic species. No reversible reactions take place. The fluxes of $\text{HNO}_3\text{(g)}$ and HCl(g) are equal to 0, while the flux of sulfuric acid is calculated from Equation (1). Since there is enough ammonia to neutralize any condensing sulfuric acid,

$$J_{\text{NH}_3, k} = 2J_{\text{H}_2\text{SO}_4, k}. \quad (21)$$

When the ammonia is depleted, then only sulfuric acid condenses and the aerosol will become acidic. As soon as this happens, the equations of section Acidic Aerosol apply.

(e) *Ammonium Nitrate Systems (No chloride reactions are active).* Possible salts in this subcase are $\text{NH}_4\text{NO}_3\text{(s)}$, $\text{Na}_2\text{SO}_4\text{(s)}$, $(\text{NH}_4)_2\text{SO}_4\text{(s)}$, and $\text{NaNO}_3\text{(s)}$ and gas-phase concentrations are such that neither (R-2) nor (R-3) favors chloride salt formation (Table 2). Thus, the only active equilibrium reaction is (R-1). The equilibrium concentrations used in Equation (1) to calculate the fluxes are

$$c_{\text{NH}_3}^{eq} = \frac{K_1}{c_{\text{HNO}_3}^{eq}}, \quad (22)$$

$$c_{\text{HNO}_3}^{eq} = \frac{-P + \left[P^2 + 4D'_{\text{NH}_3} D'_{\text{HNO}_3} K_1 \right]^{1/2}}{2D'_{\text{HNO}_3}}, \quad (23)$$

where

$$P = D'_{\text{NH}_3} c_{\text{NH}_3} - D'_{\text{HNO}_3} c_{\text{HNO}_3} - 2D'_{\text{H}_2\text{SO}_4} c_{\text{H}_2\text{SO}_4}. \quad (24)$$

The HCl(g) flux is 0. In the special cases where $\text{NH}_4\text{NO}_3(\text{s})$ does not exist in the aerosol phase, if evaporation of ammonia is required ($J_{\text{NH}_3} < 0$), then reaction (R-1) will not be able to achieve equilibrium. For this situation subcase (i) is applied.

(f) *Ammonium Chloride Systems (No nitrate reactions are active)*. Possible salts in this subcase are $\text{NH}_4\text{Cl(s)}$, $\text{Na}_2\text{SO}_4(\text{s})$, $(\text{NH}_4)_2\text{SO}_4(\text{s})$, and NaCl(s) , and gas-phase concentrations are such that neither (R-1) nor (R-3) favors nitrate formation (Table 2). Thus, the only active equilibrium reaction is (R-2). The equilibrium concentrations used in Equation (1) to calculate the fluxes are

$$c_{\text{HCl}}^{\text{eq}} = \frac{K_2}{c_{\text{NH}_3}^{\text{eq}}}, \quad (25)$$

$$c_{\text{NH}_3}^{\text{eq}} = \frac{-R + [R^2 + 4D'_{\text{NH}_3}D'_{\text{HCl}}K_2]^{1/2}}{2D'_{\text{NH}_3}}, \quad (26)$$

where

$$R = D'_{\text{HCl}}c_{\text{HCl}} + 2D'_{\text{H}_2\text{SO}_4}c_{\text{H}_2\text{SO}_4} - D'_{\text{NH}_3}c_{\text{NH}_3}. \quad (27)$$

The $\text{HNO}_3(\text{g})$ flux is 0. In the special cases where $\text{NH}_4\text{Cl(s)}$ does not exist in the aerosol phase, if evaporation of ammonia is required ($J_{\text{NH}_3} < 0$), then reaction (R-2) will not be able to achieve equilibrium. For this situation subcase (h) is applied.

(g) *Sodium System (Neither NH_4NO_3 nor NH_4Cl reactions are active)*. The possible solids in the aerosol phase are NaCl(s) , $\text{NaNO}_3(\text{s})$, and $\text{Na}_2\text{SO}_4(\text{s})$, and gas-phase concentrations are such that (R-1) does not favor $\text{NH}_4\text{NO}_3(\text{s})$ formation and (R-2) does not favor $\text{NH}_4\text{Cl(s)}$ formation. MADM first applies the equations of subcase (a) since condensation of $\text{H}_2\text{SO}_4(\text{g})$ will encourage

condensation of $\text{NH}_3(\text{g})$ leading to the potential formation of $\text{NH}_4\text{Cl(s)}$. However, because there are no ammonia salts initially present in the aerosol, if subcase (a) determines that ammonia should evaporate ($J_{\text{NH}_3} < 0$), then the system will be unable to achieve equilibrium with respect to (R-2) the $\text{NH}_4\text{Cl(s)}$ reaction (one cannot evaporate a nonexistent species). Reaction (R-2) is therefore removed as an active reaction. So for this subcase the ammonia flux is set to 0 ($J_{\text{NH}_3} = 0$) and only the sodium reaction (R-1) is applied. Following the same derivation approach we find that

$$c_{\text{HCl}}^{\text{eq}} = K_3 c_{\text{HNO}_3}^{\text{eq}}, \quad (28)$$

$$c_{\text{HNO}_3}^{\text{eq}} = \frac{S}{D'_{\text{HNO}_3} + K_3 D'_{\text{HCl}}}, \quad (29)$$

where

$$S = D'_{\text{HCl}}c_{\text{HCl}} + 2D'_{\text{H}_2\text{SO}_4}c_{\text{H}_2\text{SO}_4} + D'_{\text{HNO}_3}c_{\text{HNO}_3}. \quad (30)$$

(h) *NaCl and Na_2SO_4 aerosol where no equilibrium reactions are active*. Aerosol salt compositions include NaCl(s) or NaCl(s) with $\text{Na}_2\text{SO}_4(\text{s})$. Gas-phase concentrations are such that $c_{\text{HCl}}c_{\text{NH}_3} < K_2$, $c_{\text{HCl}}/c_{\text{HNO}_3} > K_3$, and subcase (f) indicates that $\text{NH}_3(\text{g})$ will not condense ($J_{\text{NH}_3,k} \leq 0$). In this subcase there are no equilibrium reactions taking place and no nitrate salts in the aerosol phase can be formed. Thus $J_{\text{HNO}_3,k} = 0$ and $J_{\text{NH}_3,k} = 0$. The flux of HCl is calculated as

$$J_{\text{HCl},k} = -2J_{\text{H}_2\text{SO}_4,k}. \quad (31)$$

(i) *NaNO_3 and Na_2SO_4 aerosol where no equilibrium reactions are active*. Aerosol salt compositions include $\text{NaNO}_3(\text{s})$ or $\text{NaNO}_3(\text{s})$ with $\text{Na}_2\text{SO}_4(\text{s})$. Gas-phase concentrations are such that $c_{\text{HNO}_3}c_{\text{NH}_3} < K_1$, $c_{\text{HCl}}c_{\text{NH}_3} < K_2$, $c_{\text{HCl}}/c_{\text{HNO}_3} < K_3$, and subcase (e) indicates that $\text{NH}_3(\text{g})$ will not condense ($J_{\text{NH}_3,k} \leq 0$). In this subcase there

are no equilibrium reactions taking place and no chloride salts in the aerosol phase can be formed. Thus $J_{\text{HCl},k} = 0$ and $J_{\text{NH}_3,k} = 0$. The flux of HNO_3 is calculated from equation

$$J_{\text{HNO}_3,k} = -2J_{\text{H}_2\text{SO}_4,k} \quad (32)$$

Acidic Aerosol. In this case the system contains insufficient ammonia and sodium to neutralize the sulfate present. The system is acidic and therefore NaCl(s) , $\text{NH}_4\text{Cl(s)}$, $\text{NH}_4\text{NO}_3\text{(s)}$, and $\text{NaNO}_3\text{(s)}$ will not be present. Solids present include sulfate and bisulfate salts. In this subcase there are no equilibrium reactions taking place and $J_{\text{HNO}_3,k} = J_{\text{HCl},k} = 0$. The only inorganic species transported between the two phases are sulfuric acid and ammonia with $c_{\text{NH}_3}^{eq} = 0$.

ORGANIC MASS TRANSFER

The approach of Bowman et al. (1997) is used to represent organic mass transfer in MADM with the parameters proposed by Strader et al. (1999). For both liquid and solid particles, Equation (1) is used with c_{ik}^{eq} values calculated assuming a pseudo-ideal organic aerosol solution. The organic components are assumed to exist as an organic solution that does not absorb water. No interaction between the organic and inorganic components is considered.

MADM: MARINE AIR EXPOSED TO URBAN EMISSIONS

In this section a single cell box model with MADM is used to simulate a marine aerosol population exposed to an urban atmosphere, including the idealized production of sulfuric and nitric acids as well as ammonia emissions. Sulfuric and nitric acids are the products of $\text{SO}_2\text{(g)}$ and $\text{NO}_x\text{(g)}$ oxidation, though chemical reactions responsible for the oxidation are not included here, but

instead temporally varying inputs of the acid products are used. This example is designed to highlight the ability of the model to predict the evolution of the aerosol size/composition distribution under a variety of states, including solid and liquid and acidic and neutral particles. The example also shows the ability of the algorithm to transition between the above states. A box model is used with 10 aerosol size sections from 0.05 to 10 microns in diameter.

This scenario is loosely based upon summer conditions in southern California, simulating an air parcel starting over the ocean and moving inland for 38 h. The air parcel starts at midnight over the ocean, spends 13 h in the marine boundary layer, and then moves inland. Assumed temperature and relative humidity profiles are shown in Figure 1. In this scenario $\text{HNO}_3\text{(g)}$ production is restricted to the daytime and when the air parcel is over land. Nighttime $\text{HNO}_3\text{(g)}$ production is assumed to be 0 for this example. Uniform $\text{H}_2\text{SO}_4\text{(g)}$ production is assumed since both in-cloud oxidation and gas-phase photo-oxidation of SO_2 are important sources of sulfate. In addition, two "plumes" of $\text{NH}_3\text{(g)}$ emissions are included in this scenario to represent the emissions of waste treatment facilities near the coast and the agricultural/animal operations inland. The "emissions" scheme is shown in Figure 2.

The initial marine aerosol size distribution is shown in Figure 3. It consists of a fine mode of particles dominated by ammonium sulfate and organics and a coarse mode of sodium chloride and sodium sulfate that has been partially converted to sodium nitrate. This distribution is consistent with aerosol measurements taken at San Nicholas Island off the coast of Los Angeles (Pandis et al. 1993). The initial aerosol distribution is exposed to gas-phase concentrations of $0.3 \mu\text{g m}^{-3}$ of ammonia

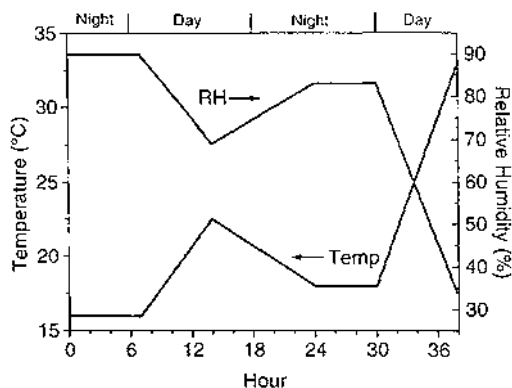


FIGURE 1. Temperature and relative humidity (RH) inputs for the MADM scenario.

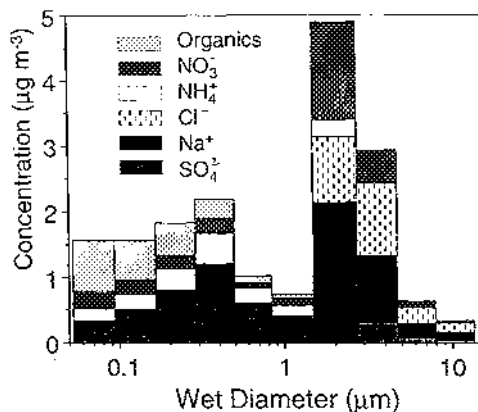


FIGURE 3. Initial aerosol composition and size distribution for the MADM scenario. Diameters are given for the wet state.

and $4.0 \mu\text{g m}^{-3}$ of nitric acid. Since there is little ammonia in the gas phase, the first hours show only the gradual displacement of chloride by nitrate in the coarse mode (sections 7–10, Figures 4a and c) and the acidification of the fine mode particles (Figure 5). Most of the nitrate is added to particles in the 1.5 to $4 \mu\text{m}$ diameter range during this period.

Diameter changes in the 10 sections are shown in Figure 6. After an hour, the $2 \mu\text{m}$

diameter particles (section 7) reach equilibrium with the gas phase, however, because the larger particles (sections 8–10) are still forming nitrate, the $2 \mu\text{m}$ diameter particles (section 7) lose $\text{HNO}_3(\text{aq})$ back to the gas phase to maintain equilibrium (Figure 7). While this process takes place, $\text{H}_2\text{SO}_4(\text{g})$ is condensing on all the particles but most rapidly on the smallest ones (Figure 4d).

At 7:00 AM sunlight begins to warm the air and reduce the relative humidity. This rise in temperature promotes the evaporation of nitrate from the fine mode sections (Figures 4 and 7), which lowers the charge ratio of acidic ions (NO_3^- , SO_4^{2-} , and Cl^-) to basic ions (NH_4^+ and Na^+) (Figure 5). By 9:30 AM, however, most of the nitrate has evaporated from the fine mode and the acid to base ratio again begins to rise. At noon the relative humidity has dropped to below the crystallization threshold of the coarse mode particles (sections 7–10, Figure 8). MADM is able to simulate cases where some of the particles are solid, some are partially solid and partially liquid, and others are liquid (Figures 6 and 8). This

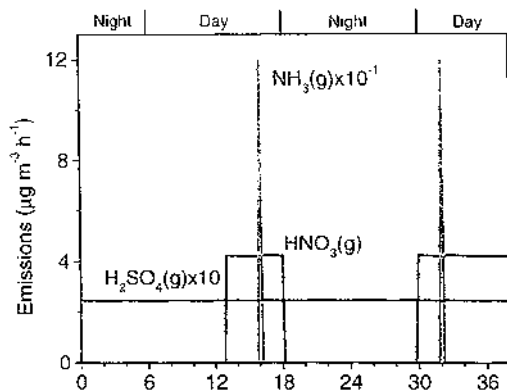


FIGURE 2. Nitric acid, ammonia ($\times 10^{-1}$), and sulfuric acid ($\times 10$) gas phase source terms for the MADM scenario.

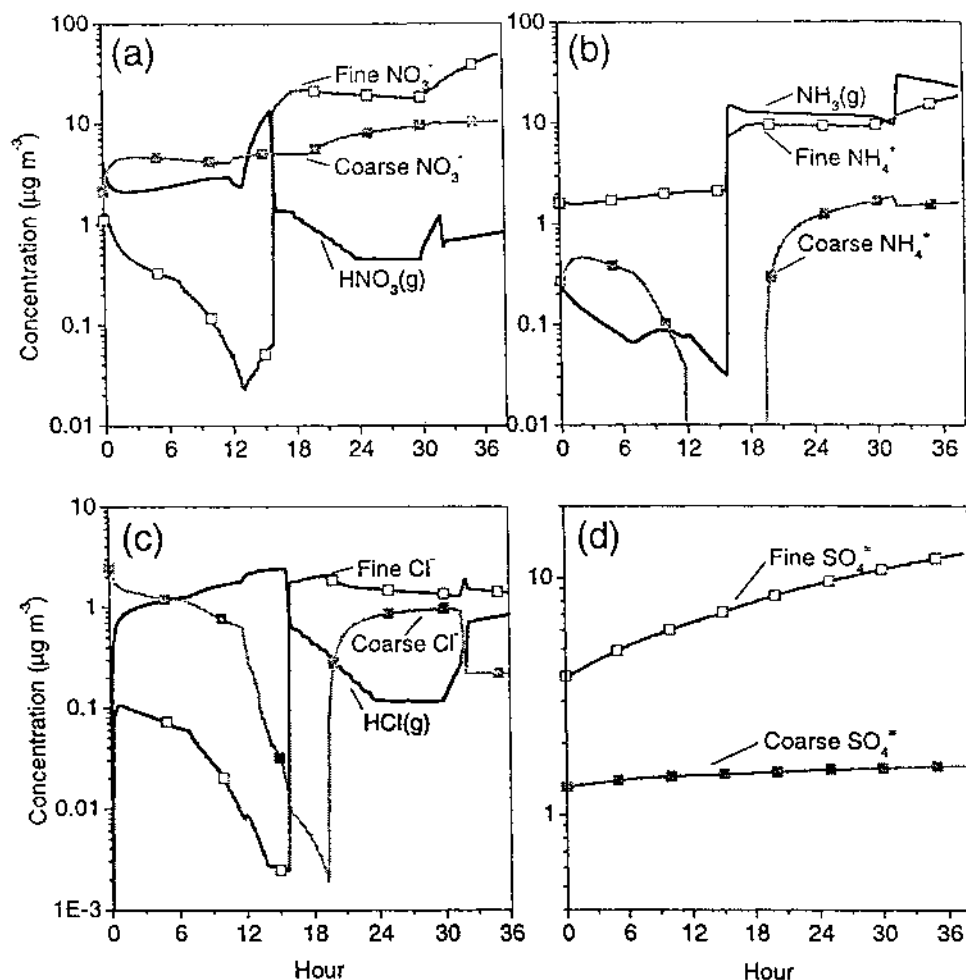


FIGURE 4. Gas and aerosol fine and coarse mode predictions of the MADM scenario for a) nitrate, b) ammonia, c) chloride, and d) sulfate. NH_4^+ completely evaporates from the coarse mode between hours 12 and 16.

change in state allows release of a small amount of NH_3 ($0.04 \mu\text{g m}^{-3}$; Figure 4b) from the coarse particles. This ammonia is rapidly taken up by the small particles and causes a 1% decrease in the acid to base ratio (Figure 5). After this, there is almost no NH_3 available in the gas phase to neutralize the condensing H_2SO_4 . The result is a steady rise in the acid:base ratio of the

small sections. Until this point, Figure 5 shows equivalent acid:base ratios for all the fine mode sections. This indicates that these particles are all maintaining equilibrium with the gas phase despite different rates of $\text{H}_2\text{SO}_4(\text{g})$ accumulation. However, after 12:00 separation becomes apparent in Figure 5 as the smaller particles are becoming acidic faster than the larger particles in the

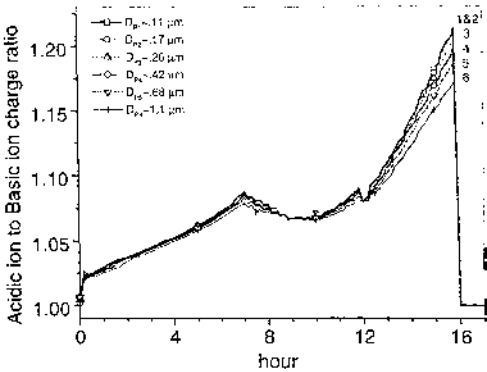


FIGURE 5. The predicted ratio of negative charge from acidic ions (NO_3^- (aq), SO_4^{2-} (aq), and Cl^- (aq)) to positive charge from basic ions (NH_4^+ (aq) and Na^+ (aq)) for fine mode (sections 1–6) during the first 17 h of the MADM scenario. The scenario average diameters, D_p , of aerosol sections 1–6 are indicated in the legend. To calculate this ratio all aerosol nitrate is assumed to exist as NO_3^- (aq), all aerosol sulfate (including bisulfate) is assumed to exist as SO_4^{2-} (aq), all aerosol chloride is assumed to exist as Cl^- (aq), all aerosol ammonia is assumed to exist as NH_4^+ (aq), and all sodium is assumed to exist as Na^+ (aq).

fine mode. In addition to the loss of the ammonia when the large particles become dry, NaCl(s) is replaced by $\text{NaNO}_3\text{(s)}$ with particles of diameters 1.2, 2.2, and 3.6 microns running out of chloride at hours 12.3, 13.5, and 14.2, respectively.

At 1:00 PM (hour 13), when the air parcel reaches land, emission of NO_x and production of $\text{HNO}_3\text{(g)}$ are assumed to begin. Because of the acidity of the small particles and the depletion of chloride in the large particles, the majority of the emitted $\text{HNO}_3\text{(g)}$ accumulates in the gas phase (Figure 4a) with a small fraction condensing on the fine particles (Figure 7).

At hour 16 (4:00 PM), the air parcel encounters the first major $\text{NH}_3\text{(g)}$ source. This results in a rapid and complete neutralization of the acidic particles (Figure 5). Uptake of the accumulated $\text{HNO}_3\text{(g)}$ and the newly emitted $\text{NH}_3\text{(g)}$ is most rapid in

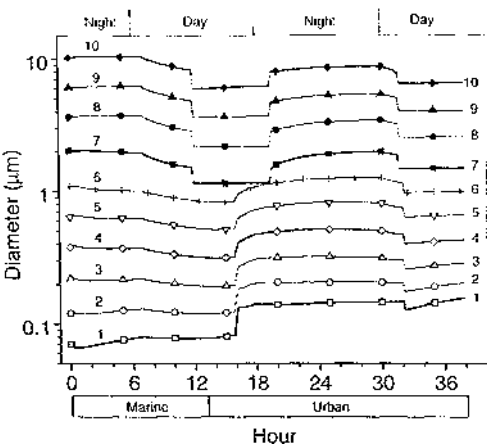


FIGURE 6. Predicted diameter changes for the 10 aerosol size sections of the MADM scenario. Sharp diameter changes indicate deliquescence (increases) and crystallization (decreases). Day and night, and periods in which the air parcel is over water (Marine) and over land (Urban), are indicated.

the smallest sections. These sections come to equilibrium with the gas phase before the larger sections. The slow down in the transfer of $\text{HNO}_3\text{(g)}$ onto the smallest sec-

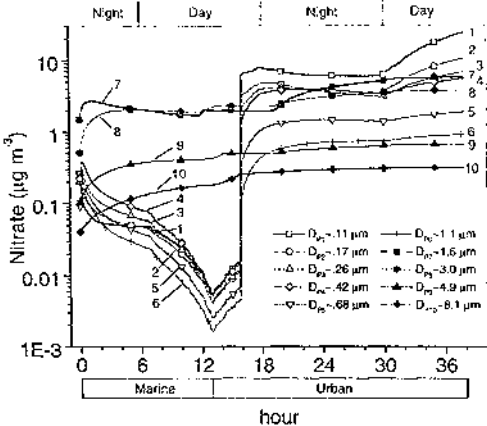


FIGURE 7. Predicted aerosol nitrate concentrations in each of the 10 sections for the MADM scenario. The scenario average diameters, D_p , of the 10 aerosol sections are indicated in the legend. Day and night, and periods in which the air parcel is over water (Marine) and over land (Urban), are indicated.

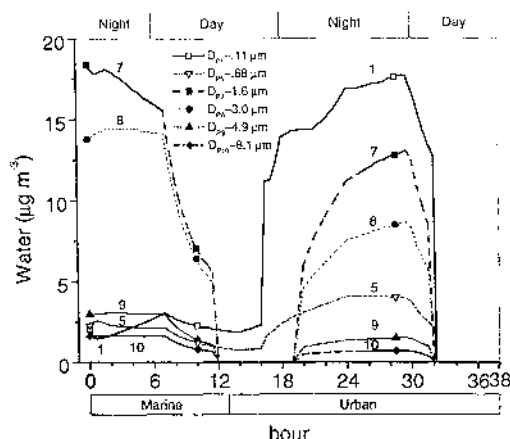


FIGURE 8. Predicted aerosol water concentrations in the MADM scenario. A zero concentration of water indicates a solid particle. The scenario average diameters, D_p , of the aerosol sections are indicated in the legend. Day and night, and periods in which the air parcel is over water (Marine) and over land (Urban), are indicated.

tion seen in Figure 7 is due to the reduction in the gas-phase concentrations of NH_3 and HNO_3 (Figures 4b, a) caused by their condensation onto the larger sections. With the increase in $\text{NH}_3(\text{g})$ concentration, the accumulated $\text{HCl}(\text{g})$ also condenses (Figure 4c).

At hour 18 (6:00 PM), the $\text{HNO}_3(\text{g})$ production ceases. This halts the condensation of $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$ onto particles $< 0.3 \mu\text{m}$ in diameter. However, the larger sections are still not in equilibrium with gas phase HNO_3 and NH_3 . Therefore, particles $> 0.3 \mu\text{m}$ in diameter continue to absorb $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$. This decreases the corresponding gas-phase concentrations and requires evaporation of these species from sections 1 and 2. Since 2:00 PM, the air has been cooling and the relative humidity rising. At 7:30 PM the coarse mode sections deliquesce (Figure 8) and begin to attract $\text{HNO}_3(\text{g})$, $\text{NH}_3(\text{g})$, and $\text{HCl}(\text{g})$ (Figure 4). This reforms NaCl in the coarse mode particles (sections 7–10) and allows for the accelerated uptake of $\text{HNO}_3(\text{g})$ in these sections as NaCl is once again converted into NaNO_3 .

As the sun rises on the second day (hour 30), $\text{HNO}_3(\text{g})$ production resumes. In addition, the relative humidity begins to drop rapidly. With the availability of $\text{HNO}_3(\text{g})$,

aerosol phase NH_4NO_3 forms (Figures 4a, b). At 7:40 AM of day 2 (hour 31.7), the coarse mode particles (sections 7–10) become dry (Figure 8). At 8:00 AM the air parcel passes over the second NH_3 source. Ten minutes later, the relative humidity is low enough that all the aerosol sections crystallize. The remainder of the simulation involves formation of $\text{NH}_4\text{NO}_3(\text{s})$ and $(\text{NH}_4)_2\text{SO}_4(\text{s})$ in all the aerosol sections, with section 1 (surface area: $\sim 69 \mu\text{m}^2 \text{cm}^{-3}$) reacting fastest and section 10 (surface area: $\sim 0.24 \mu\text{m}^2 \text{cm}^{-3}$) receiving the least secondary material.

This MADM simulation requires 19.8 CPU min on a HP C100 series workstation or an average of 31.2 CPU s per simulation h. The corresponding consumption for a Pentium PC (400 MHz) was 18.2 CPU min for the full simulation. Yet, CPU expense is not distributed evenly over the simulation (Figure 9). Sixty-five percent of the CPU time was spent between hours 13 and 16 when the fine mode particles are acidic and concentrations of $\text{NO}_3^-(\text{aq})$, $\text{Cl}^-(\text{aq})$, and $\text{NH}_3(\text{g})$ are very small ($\text{NO}_3^-(\text{aq}) < 0.016 \mu\text{g m}^{-3}$; $\text{Cl}^-(\text{aq}) < 0.001 \mu\text{g m}^{-3}$; $\text{NH}_3(\text{g}) < 0.062 \mu\text{g m}^{-3}$). Only 1% of CPU time was spent after hour 16 when $\text{NH}_3(\text{g})$ in particular is plentiful ($\text{NH}_3(\text{g}) > 9 \mu\text{g m}^{-3}$). The CPU requirements were insensitive to

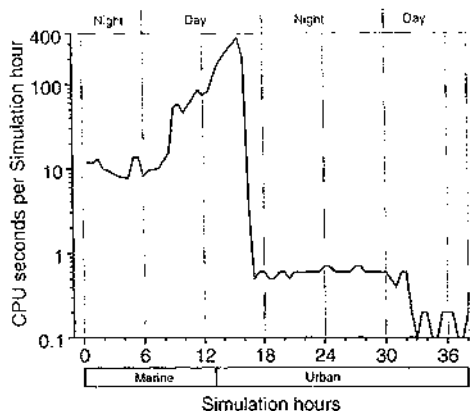


FIGURE 9. CPU expense (in seconds for a HP C100 series workstation) averaged over an hour of simulation time (plotted every 30 min). Day and night, and periods in which the air parcel is over water (Marine) and over land (Urban), are indicated.

the choice of A for values in the range between 0.05 and 2 s^{-1} . The choice of the relative tolerance had a significant effect on the CPU time, with acceleration by a factor of four for an increase of the tolerance from 10^{-5} to 10^{-3} . The error introduced by the higher tolerance was less than a few percent. Because of its CPU requirements the present version of MADM is appropriate only for box and one-dimensional trajectory models.

SUMMARY

In this work, the MADM is presented as a method for simulating the dynamic transfer of semivolatile species between the gas and aerosol phases. The novelty of this approach is its use of electroneutrality constraints to define the species flux to solid particles and to add stability and decrease stiffness in liquid particle flux calculations. This method is demonstrated to be capable of transitioning between aerosol states including the deliquescence and crystallization of the particulate phase and the transi-

tion between acidic and near-neutral conditions. MADM is able to simulate cases where some of the particles are solid, some are partially solid and partially liquid, and others are liquid.

By using MADM to describe the transition between marine and urban environments, the rates of mass transfer between the gas phase and aerosol particles of different sizes and compositions can be quantified. In addition, MADM can be used to show how diurnal temperature and relative humidity changes drive mass transfer of semivolatile species between the gas and aerosol population. This work suggests that the aerosol population often does not achieve steady-state concentrations on the time scale of changes in emissions, temperature, and relative humidity. This agrees with the conclusions of Wexler and Seinfeld (1990) and Meng and Seinfeld (1996).

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